CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF BOTTOM ASHES FROM A MUNICIPAL SOLID WASTE INCINERATOR IN NORTHERN ITALY, AIMED AT INERTIZATION AND REUSE

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RECYCLING AND REUSE OF BOTTOM ASHES FROM MUNICIPAL SOLID WASTE THERMOVALORIZATION PLANT

Municipal solid waste after the treatment in the TRM plant are:

20% BOTTOM ASHES (BA) 2% FLY ASHES (FA)

Today

BA are taken by specialized Societies and converted mostly in secondary raw materials, available only if included in other matrices (problem of the release of chemical species in the environment)

MSWI PLANT OF TURIN

The plant is working since 2014 and burn about 500.000 t of waste per year, with three lines of combustion, and a total capacity of 67,5 tons/h, at a firing peak temperature of some 1000 °C.

1.SAMPLING+REDUCTION

2.TEXTURE ANALYSIS AND MORPHOMETRIC DEFINITION

3.CHARACTERIZATION

1.SAMPLING+REDUCTION

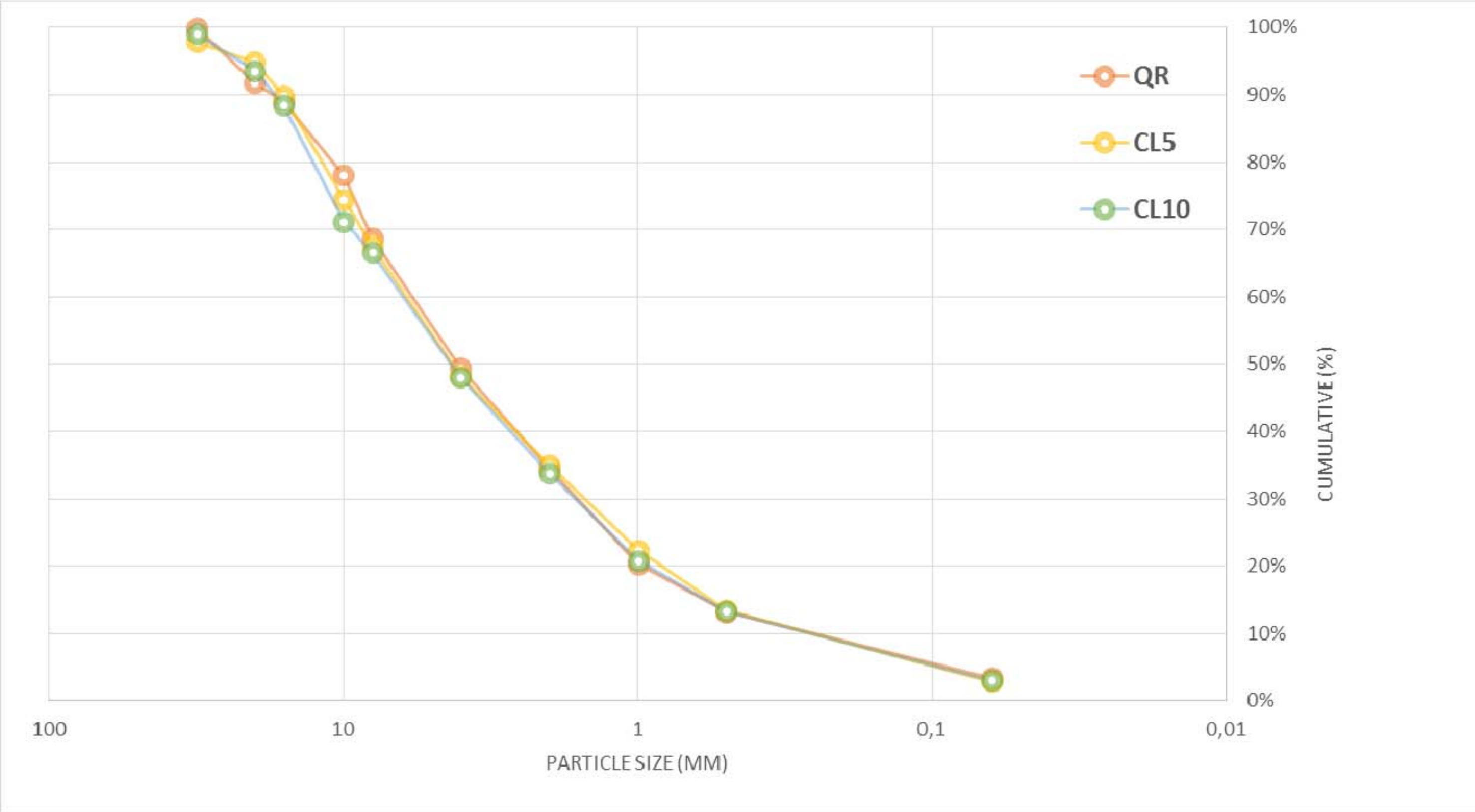
Sampling of material in the TRM plant from a falling stream

Reduction by riffle splitter
(European normative CEN/ TR- 15310 – 3 for waste characterization)

Quartering to produce **subsamples (3)**

2.TEXTURE ANALYSIS AND MORPHOMETRIC DEFINITION

Cumulative % calculated as:
(Total weight – Retained weight)/Total weight x 100).



Grain size (mm)	Retained (%)
20	8,20%
16	2,73%
10	11,00%
8	9,30%
4	19,34%
2	14,90%
1	14,15%
0,5	7,18%
0,063	9,77%
<0,063	3,42%

The three subsamples, *QR, CL5 and CL 10* show the same grain size distribution

3.CHARACTERIZATION

CHEMICAL COMPOSITION

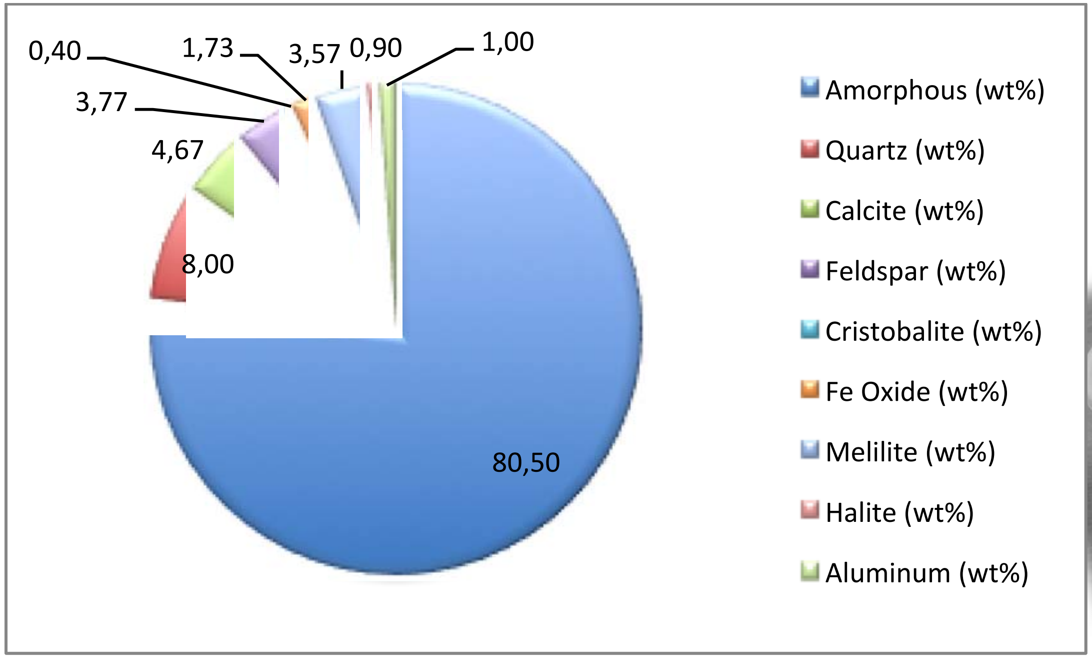
CHEMICAL AND MINERALOGICAL DETERMINATION

- XRF
- ICP/OES+MW DISSOLUTION
- SEM-EDS
- X-RAYS DIFFRACTION
- THERMOGRAVIMETRY

RELEASE TESTS

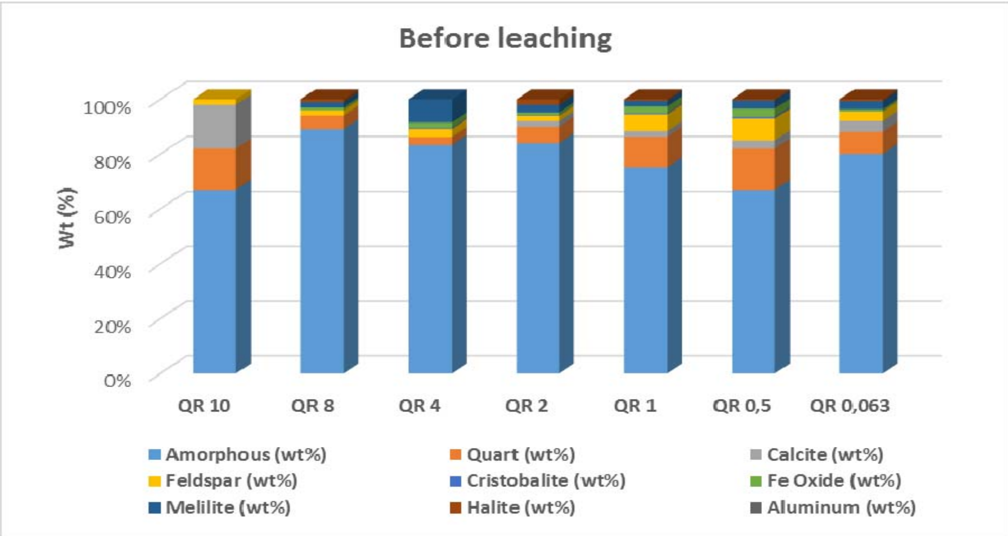
- LEACHING TESTS WITH CONDUCTIVITY LOGS
- ICP-OES AND CHROMATOGRAPHY ANALYSIS OF LEACHATES

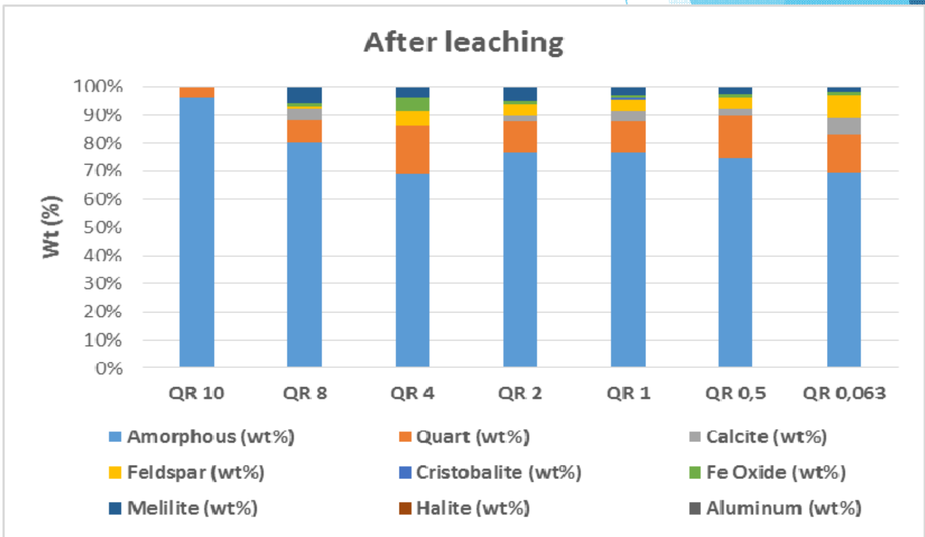
CRYSTALLINE PHASES: XRD ANALYSIS



X-RAYS DIFFRACTION, WITH GRAIN SIZE DIFFERENTIATION (BEFORE AND AFTER LEACHING)

X Ray Powder diffraction data was collected by means of a PANalyticalX'Pert Pro Bragg Brentano (θ/2θ) diffractometer



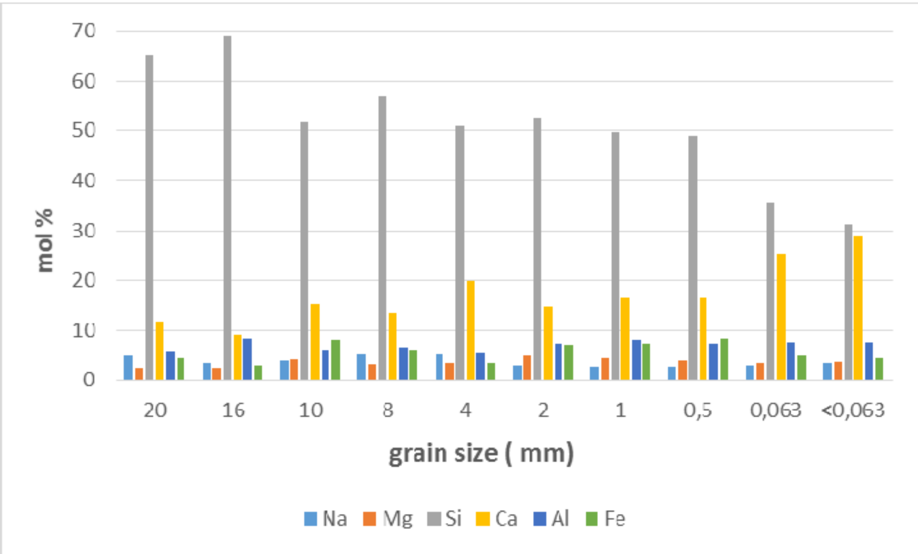


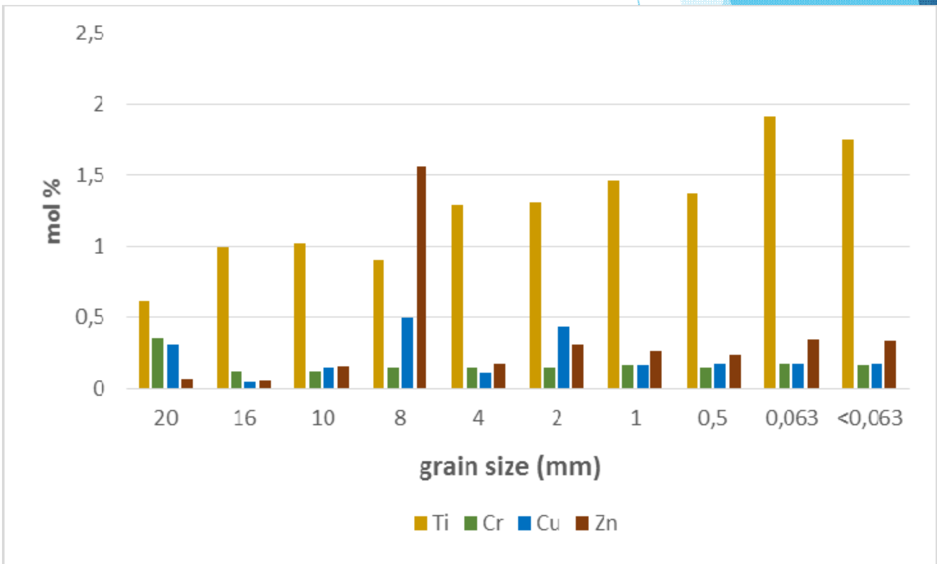
All the samples contain a large amount of an **amorphous phase** (> 50 wt%) with minority phases as quartz, calcite (except in QR 8 and 4) and feldspar (except in QR 16). **Cristobalite, Fe oxide (hematite or magnetite), melilite and halite were found as traces** in samples with grain size lower than QR 10. The presence of crystalline phases as **melilite** proved the reaching of high temperature during the firing process of the waste

All the samples present a **decreased amount of the amorphous phase.** Probably the leaching process mainly acts on the amorphous phase because this is not crystalline and then particularly reactive. This process has been proved to interest mainly the amorphous phase rather than the crystalline phases (except for the halite, which is dissolved

MOLAR COMPOSITION
(WITH GRAIN SIZE DISCRIMINATION)

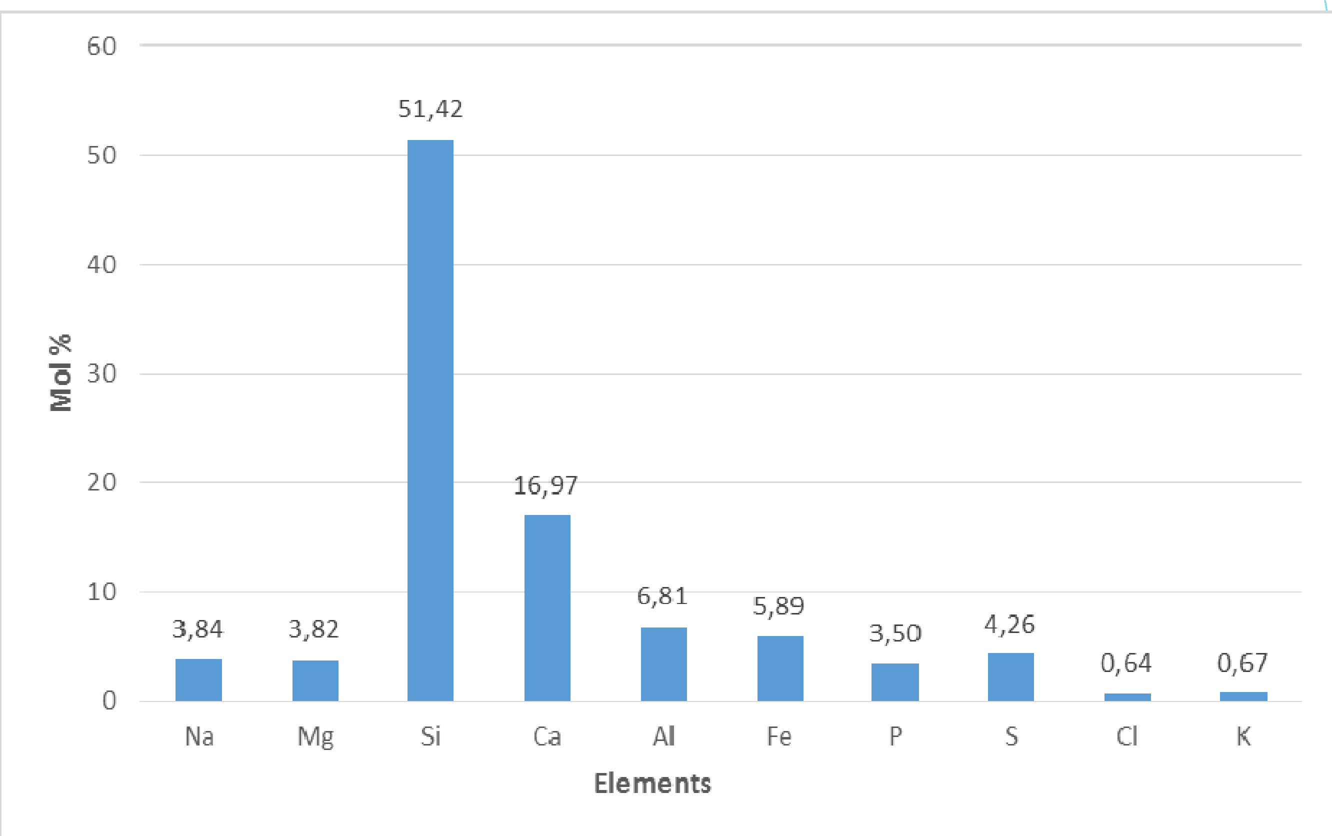
Chemical composition of BA was determined by combining data from μ-XRF, SEM-EDS and ICP-OES after microwave digestion in nitric acid. The observed chemical species are Si, Ca, Al, Fe, P, S, Cl, K, Ti, V, Cr, Mn, Ni, Cu, Zn, As, Sr and Pb, as reported in the figures, in terms of elemental molar percentages. Si, Ca, Al, Fe, Mg, Na and K (in order of abundance) are the major occurring species. The highest concentrations of heavy metals, save iron, are due to Cr, Ti, Zn and Cu. Si decreases upon decreasing grain size, while Ca increases





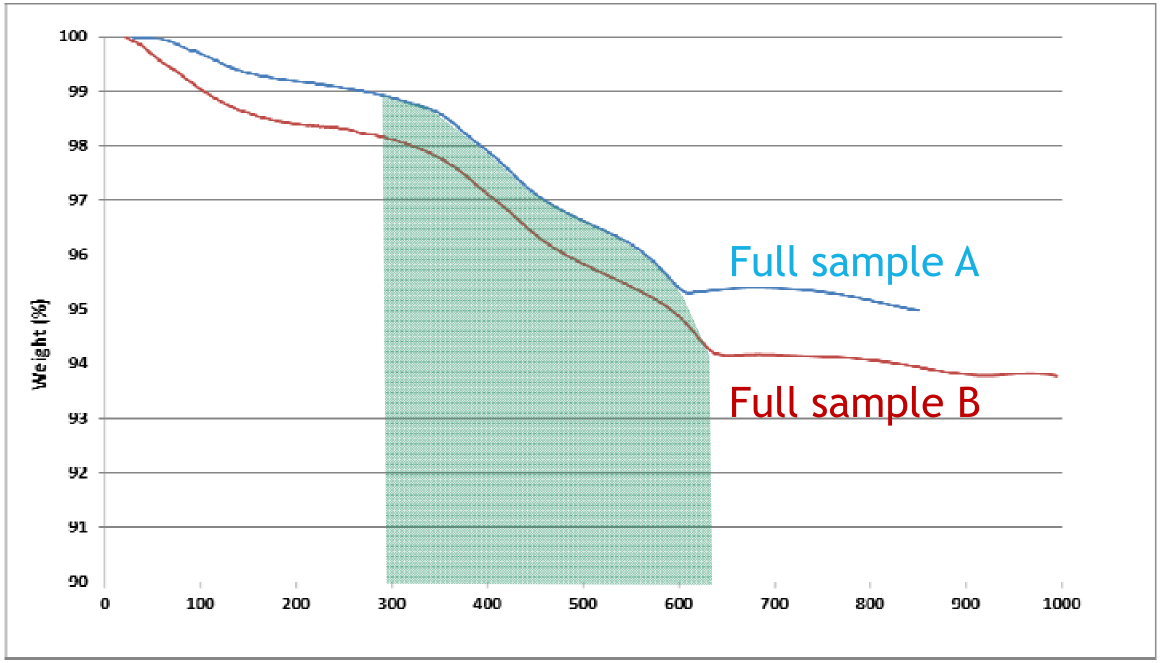
Si decreases upon decreasing grain size, while Ca increases

OVERALL MOLAR COMPOSITION (NO GRAIN SIZE DISCRIMINATION)

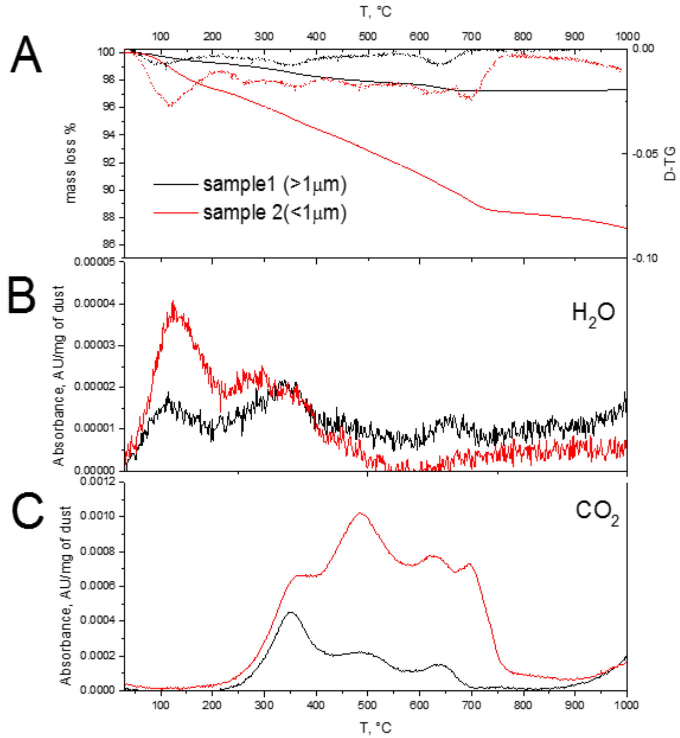


Overall composition (*XRF + microwave digestion values*) of bottom ashes.
Average values calculated without grain size discrimination.

THERMOGRAVIMETRIC ANALYSIS



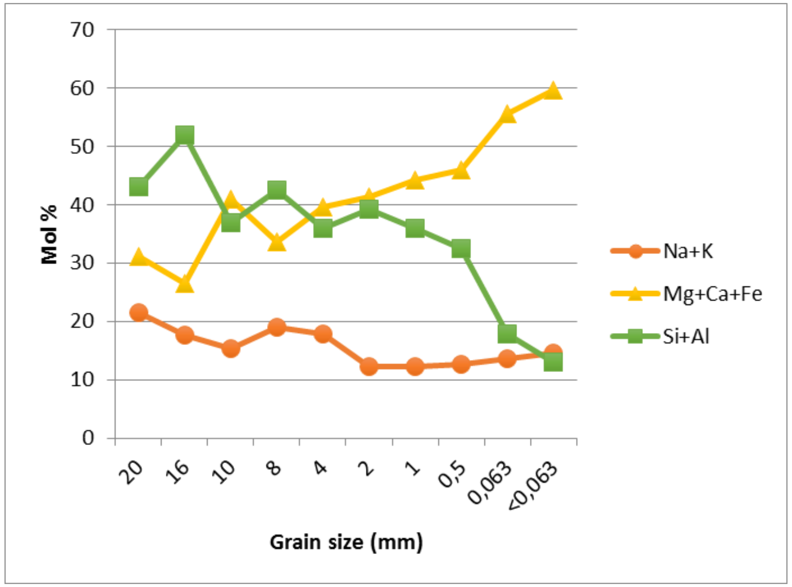
Thermogravimetric analyses (full sample) show there is a very low loss of material at about 100 °C (dehydration) and between 300 and 600 °C (probably "plastic" combustion) and a process of burning yielding a 5-6 % by weight loss that is completed at about 600 °C.



TG and DTG analyses in combination with IR-determination of volatile emissions, for bottom ashes > 1mm (black) and < 1mm (red).

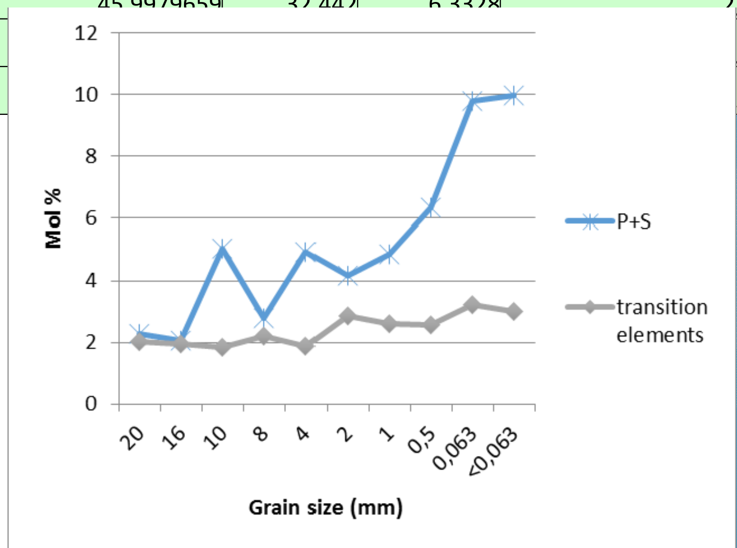
OVERALL MOLAR COMPOSITION OF THE AMORPHOUS PHASE

Overall composition of the amorphous phase obtained by subtraction of the molar composition of the main crystalline phases from XRD analysis (quartz, calcite, plagioclase, Fe-oxides, gehlenite, halite) from the overall composition of bottom ashes (> 1 mm and < 1 mm grain sizes).



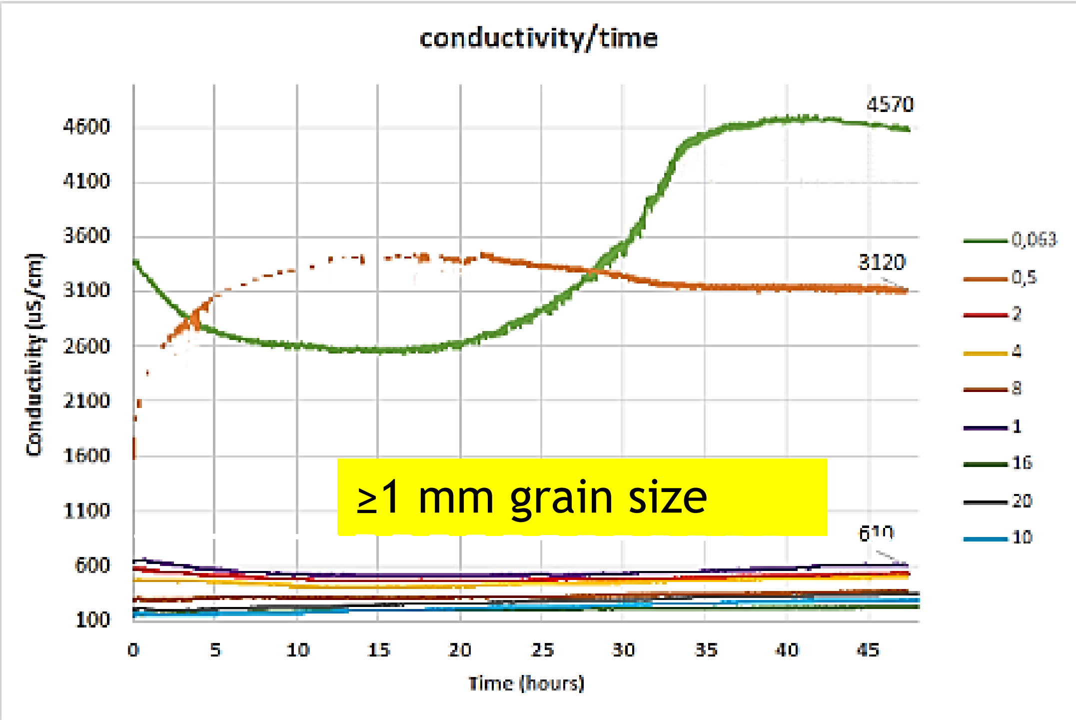
	Na+K	Mg+Ca+Fe	Si+Al	P+S	transition elements
20	21,5554	31,10051122	43,028	2,2852	2,030695353
16	17,6062	26,47212748	51,913	2,0567	1,951573644
10	15,3862	40,8876383	36,828	5,0398	1,858154686
8	18,9989	33,56211132	42,435	2,796	2,207594578
4	17,7828	39,52166724	35,89	4,9267	1,878781126
2	12,3006	41,40090291	39,272	4,1528	2,873886733
1	12,312	44,29781686	35,924	4,8672	2,598909153
0,5	12,6637	45,9979659	32,442	6,3328	2,563501701
0,063	13,5316	[illegible]	[illegible]	[illegible]	,207601201
<0,063	14,4789	[illegible]	[illegible]	[illegible]	2,98648932

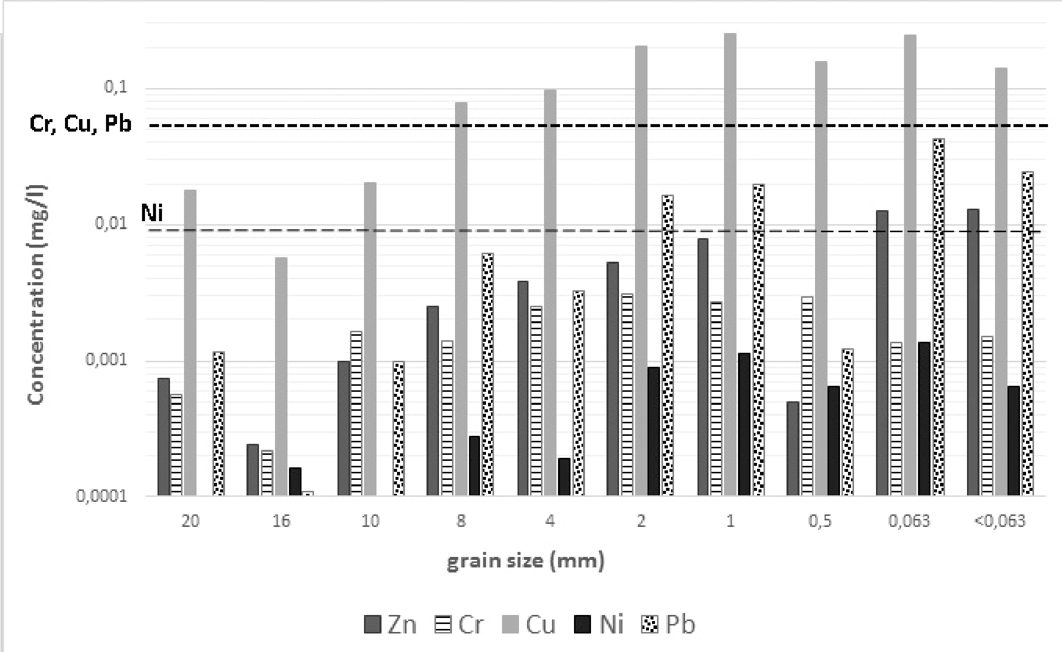
- The amorphous phase chemical composition depends on the particle size: Si+Al concentrate in large size particles, whilst Mg+Fe+Ca prefer to enter small size BA; P+S show an increase in the small particle size, especially over the range 0,063-1 mm.



LEACHING TEST AND LEACHATES ANALYSIS

European standards for the characterization of waste: **EN-12457-2** (leaching test in deionized water L/S 10/1)





Cu lies above the legal threshold values, (0,05 mg/l), settled by the European Legislations 91/156/EEC and 91/698/EEC, and transposed into the Italian law about "*not dangerous waste reuse*", D.M. 5/04/2006 n.186, ("Ministero dell'Ambiente e della Tutela del Territorio, 2006"). Pb, Cu, Ni and Zn decrease upon decreasing the grain size. Cr, Co, Cd, Ba and Zn turn out to lie below the legal threshold values.

LEACHING TEST AND LEACHATES ANALYSIS

≥1 mm

Low conductivity (< 1000 µS/cm)

pH 10-10.5

Low concentration of Cl^-(<800mg/l)

Na^+ (<800 mg/l)

< 1 mm

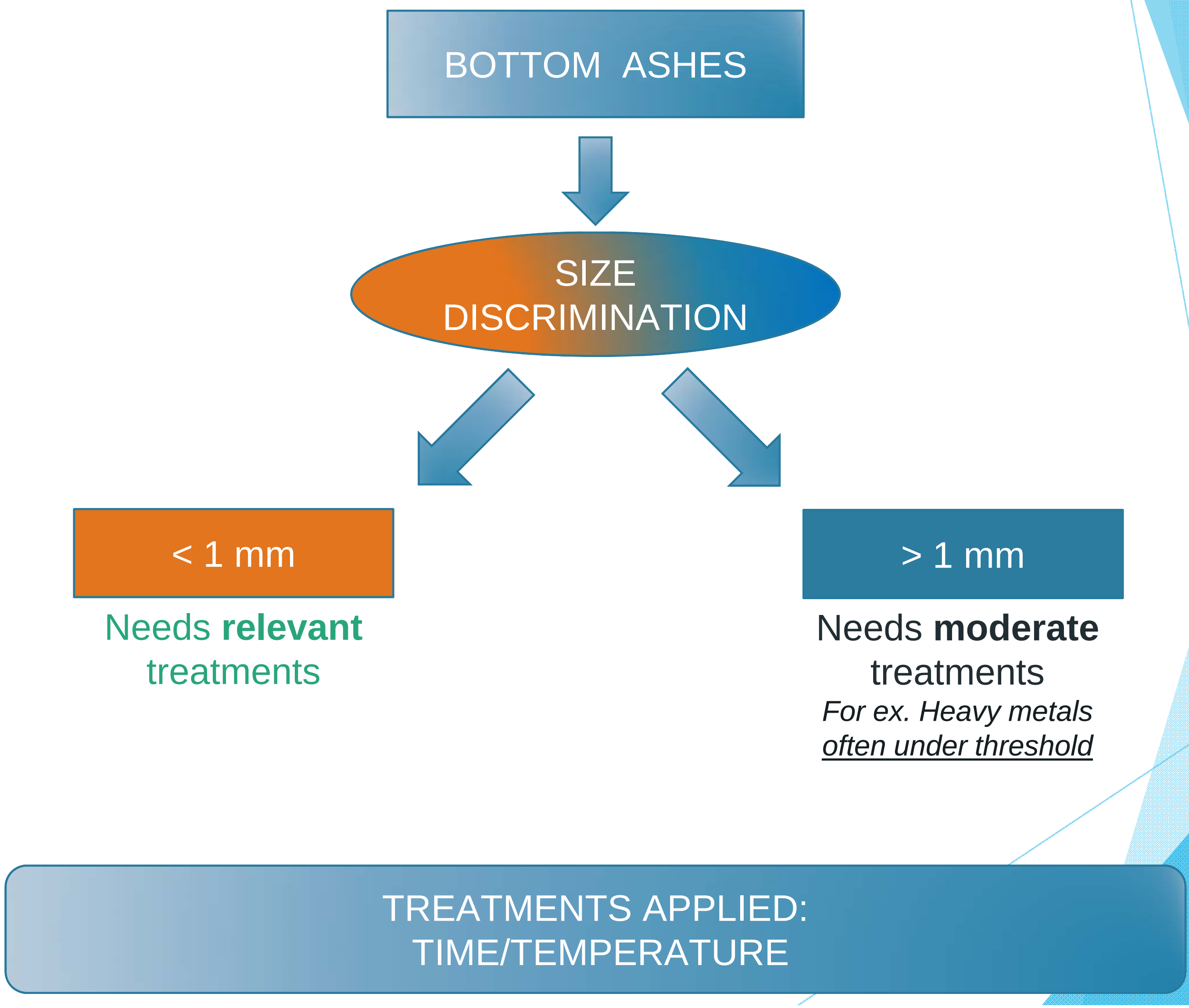
High conductivity (>4000 µS/cm)

pH 11.5

High concentration of Cl^- (up to1800 mg/l)

Na^+ (up to 950 mg/l)

The sum of the heavy metals concentrations in the leachates of BA <1 mm is more than three times larger than the one in the case of grain size ≥ 1 mm


BOTTOM ASHES
SIZE DISCRIMINATION
< 1 mm
Needs **relevant** treatments
> 1 mm
Needs **moderate** treatments
For ex. Heavy metals
often under threshold
TREATMENTS APPLIED: TIME/TEMPERATURE

CONCLUSIONS

Solid composition

- The average molar composition of the bottom ashes is represented by by 52% Si, 17% Ca, 7% Al, 6% Fe, 4% Na and Mg.

- The highest concentrations of heavy metals (mol %) are represented by Ti (1,3%), Zn (0,3%), Cu (0,2%) and Cr (0,2%); concentrated in the finer grain sizes.

- The amorphous phase is > 65 wt%, with minority phases as quartz, calcite and feldspar. Cristobalite, Fe oxide (hematite or magnetite), melilite and halite were found as <5 %
- Unburnt/partially burnt materials occur as much as some 3-4 wt%. The amorphous phase chemical composition depends on the particle size: Si+Al concentrate in large size particles, whilst Mg+Fe+Ca prefer to enter small size BA; P+S show an increase in the small particle size, especially over the range 0,063-1 mm.

- The average molar composition of the amorphous phase and Ksp of heavy metals was determined: (Na + K) 16 mol%, (Mg + Ca + Fe) 42 mol%; (Si + Al) 35 mol %; (P + S) 5 mol %; transition elements 2 mol%.

CONCLUSIONS

Leachates composition

Leaching treatments lead to an average mass decrease of about 15-20 %wt of the solid, according to the trend that the larger the particle size, the smaller the weight loss.

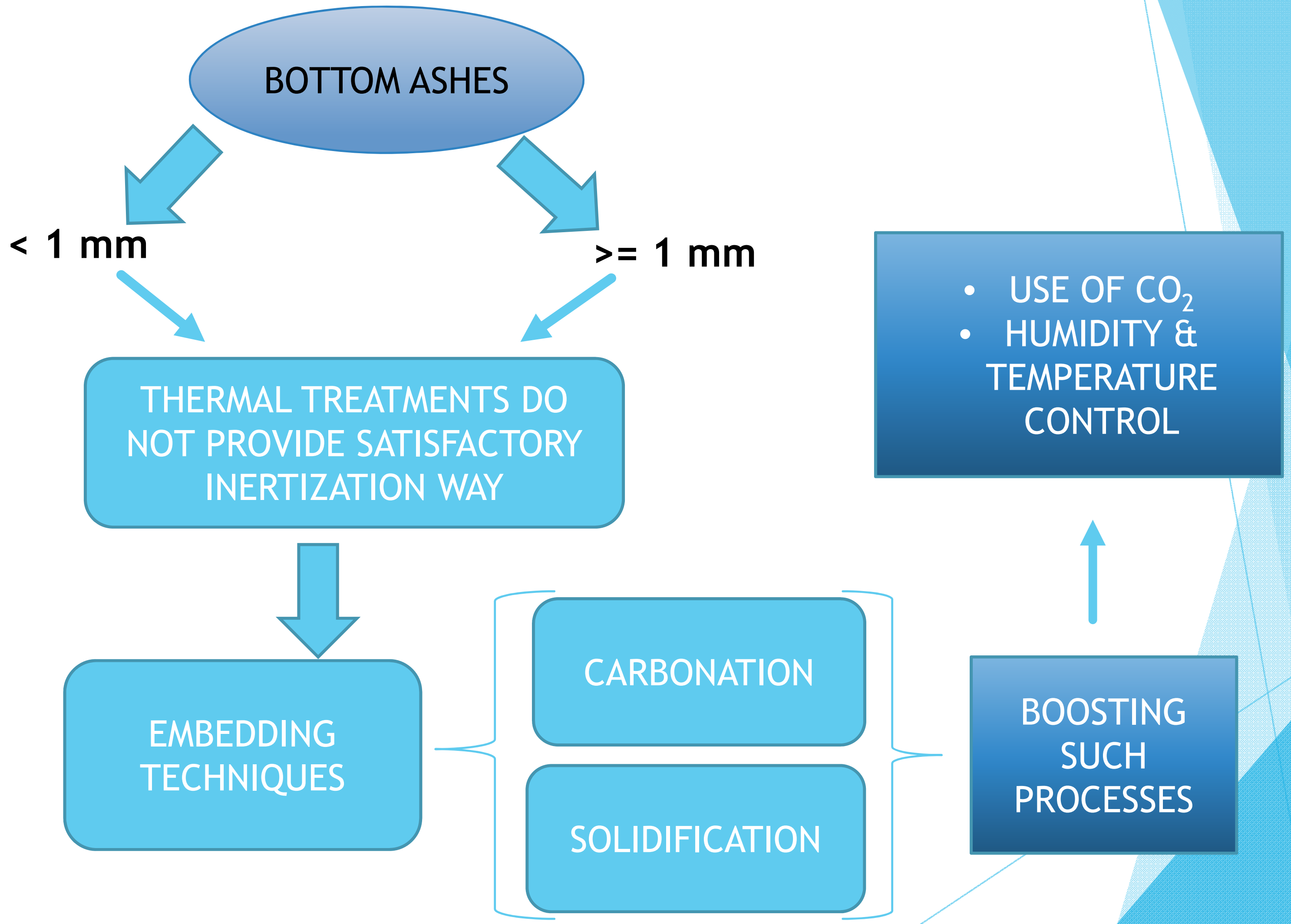
Electrolytic conductivity observations in combination with chemical composition determination of BA suggest to split bottom ashes into two classes, *i.e.* ≥ 1 mm and <1 mm.

≥ 1 mm exhibits: electrolytic conductivity (<1000 μS/cm), pH ~10-10.5, lower concentrations of Cl^- (<800 mg/l), Na^+ (<500 mg/l)
<1 mm : electrolytic conductivity up to 4000 μS/cm), pH ~11-11.5, higher concentrations of Cl^- (up to 1800 mg/l), Na^+ (up to 950 mg/l).

Moreover the sum of the heavy metals concentrations in the leachates of BA <1 mm is more than three times larger than the one in the case of grain size ≥ 1 mm

CONCLUSIONS

- Exploiting the particle size dependence of bottom ashes is necessary to design possible inertization treatments or reuse.
- We suggest grain size separation at 1 mm, relying upon electrolytic and exchanging/release activities.
- Given that most chemical species exchanging activity is affected by the amorphous phase, it is necessary to engender its vitrification or decomposition into stable oxides.


BOTTOM ASHES
< 1 mm
>= 1 mm
THERMAL TREATMENTS DO NOT PROVIDE SATISFACTORY INERTIZATION WAY
EMBEDDING TECHNIQUES
CARBONATION
SOLIDIFICATION
BOOSTING SUCH PROCESSES
USE OF CO_2
HUMIDITY & TEMPERATURE CONTROL